

Precipitation of Aluminum Basic Salts by Means of Urea

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

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Ning Kang Tang
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This work was undertaken at the suggestion of and under the direction of Professor H. H. Willard, to whom the Author wishes to express his gratitude.



A Study of the Precipitation of Aluminum Basic Sulfate by Urea¹

BY HOBART H. WILLARD AND NING KANG TANG²

In the separation of metals by precipitation as hydroxides, hydrous oxides or basic salts, the necessity for a careful control of pH is obvious. Sufficient attention has, however, not been given to the advantage of keeping the solution homogeneous with respect to pH . If the pH becomes too high locally, as, for example, by the addition of a base, even a weak one, the precipitation of some other hydroxide is facilitated, and if this occurs it may not dissolve when the solution is thoroughly mixed. Yet this is the usual method of precipitation. The best method of accomplishing this result is by the use of a substance which, dissolved in the solution, will slowly decompose so as to bring about neutralization of the acid. The following types of reagents have been used in an attempt to maintain the proper pH : buffers, such as acetic acid and acetate; insoluble oxides and carbonates, such as zinc oxide; weak bases, mostly organic, such as phenylhydrazine and pyridine; compounds which decompose with liberation of ammonia, such as hexamethylenetetramine and potassium cyanate; substances which decompose in hot solution with the formation of a volatile acidic constituent, such as sodium thiosulfate and ammonium nitrite; mixtures of halides, halates and halogen acids, such as iodate and iodide, bromate and bromide, bromate and chloride.³

(1) Original manuscript received January 30, 1934.

(2) Rockefeller Foundation Fellow. From a dissertation presented by N. K. Tang in 1930 to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) For the sake of brevity a review of the literature has been omitted, but is given in the dissertation.

Although compounds and mixtures like those above possess certain advantages, none of them fulfils simultaneously the requirements of homogeneity of solution, slow precipitation and easy control of the final pH in an entirely satisfactory manner.

Precipitation by Means of Urea. Advantages.—The fact that urea decomposes into carbon dioxide and ammonia, when its solution is heated, has long been known. Since it is very soluble in water, and its rate of decomposition

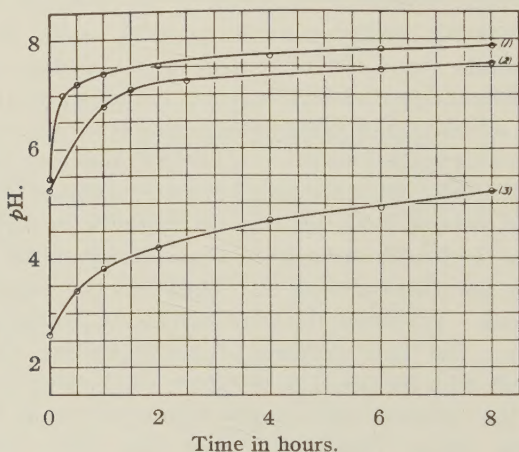


Fig. 1.—The effect of duration of heating on the pH of the solution: curve 1, solutions contained 4 g. of urea and 10 g. of ammonium chloride in 500 ml.; curve 2, solutions contained 4 g. of urea, 20 g. of ammonium chloride and 1 g. of ammonium sulfate in 500 ml.; curve 3, solutions contained 4 g. of urea, and 10 g. of ammonium chloride and 5 g. of succinic acid in 500 ml.

into ammonia and carbon dioxide, which is relatively slow, is dependent upon the temperature and duration of heating, a good control of the pH of the solution is possible, especially if it is buffered. The increase in pH can be stopped at any time by simply cooling, since no decomposition of urea takes place in the cold. The pH of the solution cannot rise very high and the more basic elements will not be precipitated, since the ammonia produced is driven from the hot solution

if the pH is much above 7. The slow evolution of carbon dioxide, produced by the decomposition of the urea, effectively prevents bumping. In such a solution the change in pH will be uniform throughout, insofar as the temperature is the same, and no local excess of the reagent will be present at any point. No undesirable foreign ion will be introduced, except in some cases that of the buffer, and the excess of the precipitant can be decomposed easily. This greatly facilitates the use of the filtrate for further determinations if desired.

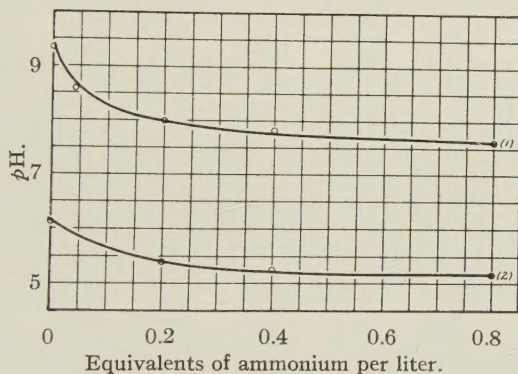


Fig. 2.—Effect of ammonium ion concentration on the pH of the solution: curve 1, solutions contained 4 g. of urea in 500 ml.; curve 2, solutions contained 4 g. of urea and 5 g. of succinic acid in 500 ml.

Consequently, if to an acid solution of an element, the hydroxide or basic salt of which is insoluble, urea is added and the mixture is heated, the hydroxide or basic salt should be precipitated slowly and uniformly throughout the solution. Precipitates formed in this manner should, in general, be more granular and less prone to show co-precipitation phenomena, thus giving better separations, a fact not previously emphasized.

The Effect of Duration of Heating on the pH of a Solution of Urea Containing Ammonium Salts and Succinic Acid.—The materials indicated were dissolved in 500 ml. of water and heated in an Erlenmeyer flask, covered with a watch glass, by immersion in boiling water. At intervals, samples were withdrawn, cooled in

running water, and the pH in these and subsequent experiments determined by using a quinhydrone electrode for values below 8, and a hydrogen electrode for those above. The curves in Fig. 1 show the relationships obtained.

The Effect of the Concentration of Ammonium Ion on the Final pH Attained by Heating Solutions of Urea.—Two series of solutions were prepared, each containing 4 g. of urea, together with

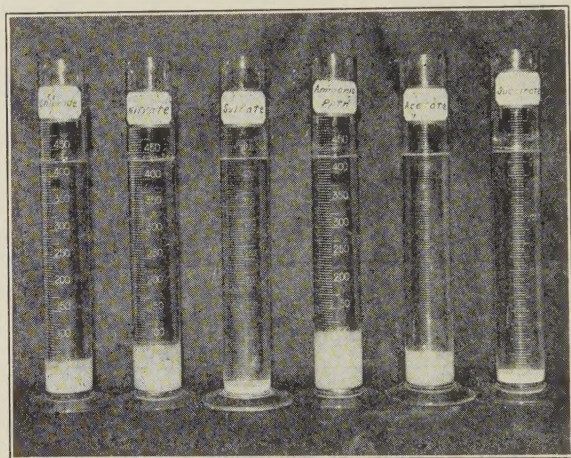


Fig. 3.—Effect of chloride, nitrate, sulfate, acetate and succinate on the precipitate obtained by urea, and of sulfate on precipitation by ammonia.

varying amounts of ammonium chloride in 500 ml. Series 1 also contained 1 g. of ammonium sulfate while series 2 contained 5 g. of succinic acid in addition to the ammonium chloride. These were heated for ten hours in the manner given above. They were then cooled and the pH determined. Curves 1 and 2, respectively, in Fig. 2 show the results obtained.

The Influence of Various Anions on the Character of the Precipitate Obtained with Aluminum Salts.—In previous work on the precipitation of basic salts and hydroxides, no attention has been paid to the importance of the anion present in affecting the physical character of the precipitate. In some cases attention has been called to the fact that solutions of different

salts of a metal gave different results, but no systematic investigation of this subject has been made. In preliminary work it was noticed that when a solution containing alum was heated with urea, a dense precipitate was obtained. However, when the solution contained aluminum chloride instead of the alum, the precipitate was of the same gelatinous nature as that obtained by an ammonium hydroxide precipitation. A series of experiments was therefore made to determine the influence of various anions. Solutions containing aluminum chloride equivalent to 0.1 g. of aluminum, and 4 g. of urea in 500 ml. were prepared. Fifteen milli-equivalents of the anion, either as the alkali salt or the free acid, was added and the solution boiled gently over a free flame. Table I gives the results of the observations.

A similar series using 10 g. of ammonium chloride in addition to the above, to cause slower precipitation, gave precipitates which were slightly less voluminous but by no means dense, except as noted above. When the precipitation was carried out in the presence of organic anions, it was found necessary to use ammonium chloride and a larger concentration of the anion. Precipitates

TABLE I
EFFECT OF INORGANIC ANIONS ON THE CHARACTER OF THE
PRECIPITATE

Anion	Character of precipitate	Anion	Character of precipitate
Nitrate	Flocculent	Sulfate	Dense
Chloride	Flocculent	Selenite	Fairly dense
Chlorate	Flocculent	Selenate	Dense
Iodate	Flocculent	Tellurate	Flocculent
Perchlorate	Flocculent	Dithionate	Flocculent
Sulfite	Flocculent	Chromate	Flocculent

resulting in the presence of formate, oxalate, succinate, benzoate, and phthalate were dense, while that formed in the presence of acetate was flocculent. Figure 3 shows the effect of several of the above anions on the character of the precipitate.

In the precipitation of aluminum it is evident that a slow diminution of the hydrogen ion concentration by the decomposition of urea does not

necessarily produce a dense precipitate. The proper anion must be present and sulfate is particularly effective. But even this will not cause a dense precipitate unless the latter is formed by slow precipitation from a homogeneous solution. This is shown by the fourth cylinder in Fig. 3, in which sulfate was present. It seems therefore that the formation of a dense precipitate depends upon at least two factors.

A Study of the Dense Basic Sulfate Precipitate

Since the dense precipitate obtained by precipitation in the presence of certain anions is very different from the ordinary gelatinous one, a study of its physical properties and composition was made. The one formed in the presence of sulfate ion was selected for two reasons. (1) The precipitate could be obtained from solutions of widely different *pH* values. (2) The determination of the sulfate content of the precipitate could be made easily.

Effect of the Concentration of Sulfate Ion on the Quality of the Precipitate.—Solutions of 500-ml. volume, containing 0.1 g. (about 7 millimoles per liter) of aluminum, as chloride, 4 g. of urea and varying amounts of ammonium sulfate, were heated to about 90° on an electric hot-plate. The results of the observations are given in Table II.

TABLE II
THE EFFECT OF THE CONCENTRATION OF SULFATE ION ON
THE CHARACTER OF THE PRECIPITATE

Sulfate ion, mm. per liter	Quality of precipitate	Sulfate ion, mm. per liter	Quality of precipitate
0	Flocculent	1.5	Less flocculent
.02	Flocculent	2	Rather dense
.2	Less flocculent	10	Dense
1	Less flocculent	20	Dense

An entirely satisfactory precipitate was not obtained until the solution contained 10 millimoles of sulfate ion per liter. This was an amount of sulfate which was practically equivalent to the quantity of aluminum present.

Microscopic and X-ray Examination.—A mi-

croscopic examination of the dense precipitate obtained in the presence of sulfate ion showed that it consisted of independent spherical granules of almost uniform size, with no sharp edges or angles characteristic of crystals. It was entirely different from the gelatinous precipitate obtained with ammonia, which consisted of large granules of no uniformity in size or shape.

An X-ray diffraction pattern obtained from a sample of a dense precipitate containing 59.73% Al_2O_3 , 7.16% SO_3 and 33.11% H_2O showed only a few faint reflections corresponding to the monohydrate, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. From a comparison of this pattern with similar ones obtained from precipitates produced by evaporation of a diethylamine aluminate solution and by an ordinary ammonia precipitation, it was concluded that the dense precipitate either contained very little crystalline material or consisted of a crystalline mixture of such complexity that the net result was similar to that which would be obtained from amorphous material.

The Determination of the Molar Ratio Aluminum to Sulfate.—Analyses of several precipitates showed that the sulfate content varied according to the conditions of precipitation, and there was not present a definite compound. Consequently the molar ratio, Al/SO_4 , was determined in precipitates obtained under varying conditions, in order to ascertain the effect of $p\text{H}$ and the concentration of sulfate ion on that ratio and also on the physical characteristics of the precipitate. Miller⁴ studied in detail the composition of precipitates formed at different $p\text{H}$ values. He added varying volumes of standard sodium hydroxide solution to known volumes of potassium alum solution, then determined the $p\text{H}$ of the filtrates and the amounts of aluminum and sulfate in the precipitates. The results show that between $p\text{H}$ 4.0 and 5.5, the molar ratio Al/SO_4 is practically constant. At higher $p\text{H}$ values the sulfate content rapidly becomes smaller, and finally disappears completely. In the present work the Al/SO_4 ratio in the precipitates was

(4) Miller, *U. S. Pub. Health Rep.*, **38**, 1995 (1923).

studied over the *pH* range 6.5 to 9.4. The procedure was somewhat simpler than that of Miller,⁴ since (1) a standard aluminum solution was used; (2) the precipitation was complete over the above range, neglecting the small solubility at the higher *pH* values; and (3) the precipitate, being dense, was easily filtered and washed.

A solution of aluminum chloride, equivalent to 2.0 g. of the metal per liter, was prepared by dissolving the metal (99.94%) in hydrochloric acid, evaporating off the excess acid and diluting to the required volume. Fifty milliliters of this solution was transferred to an Erlenmeyer flask, 4 g. of urea and 1 g. of ammonium sulfate (or an equivalent weight of potassium sulfate for *pH* values above 8.4) added. After diluting to 500 ml. the flask was covered and heated in a water-bath at the temperature of boiling water until the desired *pH* had been reached as estimated by the duration of heating. In order to obtain a *pH* higher than 9, the ammonium salt, formed during the precipitation of the aluminum hydroxide, had to be removed. This was accomplished by decanting the supernatant liquid, adding a fresh solution of urea and potassium sulfate, and heating for ten hours. Table III shows the correlation between the time of heating such a mixture and the *pH* attained.

TABLE III
INFLUENCE OF TIME OF HEATING ON THE *pH*

Duration of heating, hrs.	<i>pH</i>	Duration of heating, hrs.	<i>pH</i>
0.66	6.5	4	8.2
1.5	7.1	6	8.4
2	7.5	4-6 ^a	8.6
2.5	7.8	10 ^a	8.8-9.0
3	8.0		

^a Potassium sulfate used instead of ammonium sulfate.

After heating, the flask was cooled in running water, the precipitate filtered off and washed fifteen times with hot, 1% ammonium chloride solution containing a trace of ammonium hydroxide. The *pH* of the filtrate was determined. The precipitate was dissolved in hydrochloric acid, the excess acid evaporated off and the solu-

tion diluted. It was neutralized to turbidity with sodium carbonate solution and cleared by the addition of a drop or two of hydrochloric acid. The sulfate was then determined gravimetrically by precipitation with barium chloride. The relationship between the pH and molar ratio Al/SO_4 is shown in Table IV and Fig. 4.

TABLE IV
MOLAR RATIO Al/SO_4 AT VARYING pH
Concentration of SO_4 0.015 M

pH	Al/SO_4 ratio	pH	Al/SO_4 ratio	pH	Al/SO_4 ratio
6.53	5.40	7.77	12.3	8.60	33.9
7.03	8.11	7.95	14.5	8.64	32.5
7.07	8.18	7.97	14.8	8.69	36.7
7.19	8.47	8.02	15.3	8.71	46.5
7.38	9.84	8.05	15.4	8.88	69.8
7.48	9.95	8.05	14.9	8.93	70.9
7.50	10.2	8.17	18.0	9.00	82.4
7.71	10.7	8.22	16.2	9.36	190
7.77	12.2	8.28	19.2	9.43	210

From the results obtained it can be concluded that: (1) precipitates obtained at the same pH have a fairly constant composition; (2) with an increase in pH , the sulfate content of the precipitate decreases but does not disappear completely even at a pH of 9.4.

The change in the Al/SO_4 ratio is accompanied by a change in the physical properties of the precipitates. Those which contain a larger proportion of sulfate, *i. e.*, obtained at a lower pH , are fine grained and more readily soluble in cold, dilute hydrochloric acid. Those which contain a smaller proportion of sulfate, *i. e.*, obtained at a higher pH , are coarser grained, less dense, and dissolve only upon prolonged digestion with fairly concentrated hydrochloric acid.

The Effect of Continuous Washing on the Composition of the Precipitate.—In order to ascertain what effect continuous washing with water would have on the dense precipitate obtained by heating with urea, a sample was prepared and washed with hot 1% ammonium chloride and air-dried. One portion of this was used to determine the Al/SO_4 ratio, and another extracted with cold water for several days in a

Soxhlet extractor. This latter was again air-dried and the Al/SO_4 ratio determined. It was found that very little change had occurred during the extraction, either in the proportion of sulfate present, or in the physical character of the precipitate. It still retained its dense granular nature and showed absolutely no tendency to become colloidal and run through the extraction thimble.

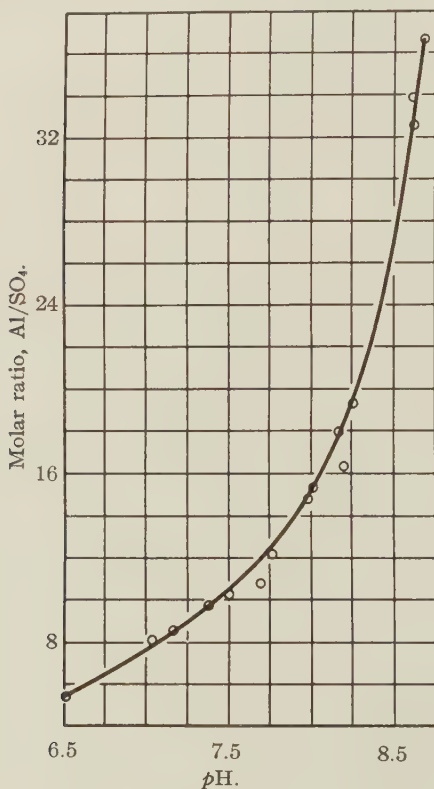


Fig. 4.—Effect of pH on molar ratio Al/SO_4 .

The Influence of Sulfate Ion Concentration on the Al/SO_4 Ratio in the Precipitate.—The procedure was the same as before except that the concentration of sulfate ion was 0.15 M instead of 0.015 M . Table V shows the results, together with ratios obtained at the same pH with a sulfate ion concentration of 0.015 M .

From this it is seen that the proportion of sul-

fate present in the precipitate is a function of the sulfate ion concentration of the solution from which the precipitation is made. At a given pH , the higher the sulfate ion concentration, the smaller the Al/SO_4 ratio, or the greater the proportion of sulfate. This would be expected either on the basis of compound formation or of adsorption. Charriou⁵ showed that when aluminum hydroxide was precipitated with ammonium hydroxide in the presence of varying amounts of ammonium sulfate, the absorption of sulfate by the precipitate followed Freundlich's law. The phenomenon of adsorption of sulfate by hydrous oxides has also been investigated by Weiser and Porter.⁶

TABLE V
THE EFFECT OF SULFATE ION CONCENTRATION ON THE
COMPOSITION OF THE PRECIPITATE

SO_4 concn., moles/l.	pH	Al/SO_4 ratio
0.015	7.38	9.84 ^a
.15	7.38	7.35
.15	7.38	7.28
.015	7.77	12.25 ^a
.15	7.78	9.75
.15	7.79	9.77

^a From data in Table IV.

Approaching the Equilibrium from Both Sides.—Since the sulfate content of the precipitate varies with the pH of the solution, it seemed well to determine whether the sulfate present in a precipitate formed at low pH would be removed by digesting in a solution of higher pH and *vice versa*. A precipitate was prepared in a solution having a pH of approximately 7, in the manner already described. The supernatant liquid was decanted and the pH determined. To the precipitate in the flask, 4 g. of urea and 1.32 g. of potassium sulfate were added and the mixture diluted to 500 ml. After heating in a water-bath for about ten hours with occasional shaking, the precipitate was filtered off. The Al/SO_4 ratio in the precipitate and the pH of the filtrate were determined. The results obtained are given in Table VI.

(5) Charriou, *J. chim. phys.*, **23**, 621 (1926).

(6) Weiser and Porter, *J. Phys. Chem.*, **31**, 1383 (1927).

TABLE VI
DECREASING THE PROPORTION OF SULFATE BY INCREASE
IN pH

pH at which ppt. was prepd.	7.08	7.13
Ratio Al/SO_4 at original pH^a	8.18	8.30
pH at which ppt. was digested	9.36	9.43
Ratio Al/SO_4 at final pH	190	210

^a From curve in Fig. 4.

It is probable that this decrease in the proportion of sulfate occurs during all precipitations of aluminum by urea in the presence of sulfate. The precipitate is formed slowly at a relatively low pH and so contains a correspondingly large proportion of sulfate, or low Al/SO_4 ratio. As the digestion is continued and the pH increases, this sulfate is lost.

To investigate the reverse process, a precipitate prepared at a high pH as described above, was filtered off and the pH of the filtrate determined. The precipitate was returned to the flask, 4 g. of urea, 1 g. of ammonium sulfate and 20 g. of ammonium chloride (to maintain a low pH) were added. The mixture was diluted to 500 ml. and heated on a hot-plate for several days, while mechanically stirred. The solution was kept at a constant volume by the occasional addition of water. The precipitate was filtered off, the ratio Al/SO_4 in the precipitate, and the pH of the filtrate determined. The results are shown in Table VII.

TABLE VII
INCREASING THE PROPORTION OF SULFATE BY DECREASE
IN pH

pH at which precipitate was prepared	9.14
Ratio Al/SO_4 at original pH^a	123
pH at which precipitate was digested	6.50
Ratio Al/SO_4 at final pH found	34.2
Ratio Al/SO_4 at final pH^a calcd.	5.40

^a From curve in Fig. 4.

The reaction involving an increase in the proportion of sulfate at lower pH evidently proceeds much more slowly than the reverse reaction, several days being insufficient for equilibrium to be reached.

Slow Precipitation by Extremely Dilute Ammonium Hydroxide.—Since the dense precipitate obtained in the manner described does not contain urea, it should be possible to form a precipitate of the same dense nature by the very slow addition of an extremely dilute ammonium hydroxide solution to one containing aluminum chloride and sulfate ion. Five hundred milliliters of solution containing 0.1 g. of aluminum, as chloride, and 1 g. of ammonium sulfate was heated to about 80° in an Erlenmeyer flask. While this solution was being stirred mechanically, 0.002 *M* ammonium hydroxide was added dropwise from a buret, over a period of several days, until the solution reacted alkaline to methyl red. The precipitate was filtered off, washed with hot 1% ammonium chloride solution and the Al/SO₄ ratio determined. The precipitate was very dense and dissolved readily in cold dilute hydrochloric acid. It had an Al/SO₄ ratio of 8.0. This shows that the precipitation by urea is merely a process of slow precipitation, and that a precipitate of similar composition and dense character can be obtained by the very slow addition of extremely dilute ammonium hydroxide. With more concentrated ammonia the results were much less successful. The fact that the time required with ammonia is so enormously greater than that with urea is doubtless due to the homogeneity of the latter solution as already mentioned.

The Solubility of the Dense Precipitate at Various *pH* Values.—The amount of aluminum remaining in solution after an ammonium hydroxide precipitation has been determined by Blum⁷ and by Jander and Weber.⁸ The former found that as much as 6 mg. of aluminum oxide per liter remained unprecipitated when the solution was just alkaline to *p*-nitrophenol (*pH* 6) while 2 mg. was left in solution when it was just alkaline to phenolphthalein (*pH* 9). The precipitation was complete in the presence of con-

(7) W. Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).

(8) Jander and Weber, *Z. anorg. allgem. Chem.*, **131**, 266 (1923).

siderable ammonium chloride, at a pH of 6.5 to 7.5, which is approximately defined by the color change of methyl red. The latter authors reported that from 7.5 to 8.75 mg. of aluminum oxide per liter remained dissolved when ammonium hydroxide was added to a hot solution, containing 16 g. per liter of ammonium chloride, until alkaline to litmus. If the precipitation was made in the cold, only 5 mg. of aluminum oxide failed to precipitate.

In the present determination, for pH values between 6.5 and 7.5, 0.1 g. of aluminum as chloride in 500 ml. of solution, containing 4 g. of urea, 1 g. of ammonium sulfate and 20 g. of ammonium chloride was gently boiled until the desired pH had been attained. For pH values around 8.4, the ammonium salts were omitted and 1.0 g. of potassium sulfate added, while solutions which were taken to about pH 9, contained 0.5 g. of potassium sulfate and only 0.01 g. of aluminum. After digestion, the solution was cooled, the precipitate filtered off and the pH of the filtrate determined. The aluminum left in solution was determined colorimetrically by the method of Winter, Thrun and Bird⁹ if 0.1 mg. or less was present. With larger quantities, the lake was filtered off, washed, ignited and the oxide weighed. The results are given in Table VIII.

TABLE VIII
SOLUBILITY OF THE DENSE BASIC SULFATE PRECIPITATE
AT VARIOUS pH VALUES

pH	Al_2O_3 , mg./l.	pH	Al_2O_3 , mg./l.	pH	Al_2O_3 , mg./l.
6.58	0.2	7.27	0.2	8.95	2.8
6.77	.2	7.50	.2	9.00	2.2
6.99	.2	8.43	.8	9.02	2.4
7.09	.2	8.85	2.6		

This shows that the solubility of the dense sulfate precipitate is of the same order as that of aluminum hydroxide obtained by Blum's method, and that most complete precipitation occurs at a pH of 6.5 to 7.5. This condition can be realized by gently boiling for two hours, the alu-

(9) Winter, Thrun and Bird, *J. Am. Chem. Soc.*, **51**, 2730 (1929).

minum solution containing 4 g. of urea and 10 to 20 g. of ammonium chloride in 500 ml.

The advantages of urea as a reagent for the precipitation of aluminum may be summarized as follows. (1) It gives a homogeneous solution in which the increase in pH comes from within. (2) The final pH is attained slowly, without attention, and can be regulated accurately. (3) The slow evolution of carbon dioxide prevents bumping. (4) Urea is relatively inert to most reagents but can be removed easily if necessary. (5) It is cheap, easily obtained and readily soluble. The application of this precipitation process to the separation of aluminum from other metals will be described in a subsequent paper.

Summary

1. The slow decomposition of urea in hot solution into ammonia and carbon dioxide has been applied to the precipitation of aluminum in the presence of various anions and under varying conditions.

2. In the presence of sulfate, selenate and a number of organic anions such as succinate, formate, benzoate and phthalate, the precipitate was dense, in other cases, flocculent. Ammonia gives a flocculent precipitate in all cases unless it is extremely dilute and added over a period of several days.

3. The proportion of sulfate in the precipitate increased with decrease in pH and to a much smaller extent, with increase in sulfate concentration. At the same time there was an increase in the apparent density of the precipitate and in its solubility in acids. Washing with water had no effect.

4. Long digestion in a hot solution of different pH changed the proportion of sulfate in the direction to be expected.

5. The solubility of the basic sulfate is 0.2 mg. of aluminum oxide per liter at pH values between 6.5 and 7.5, but increases beyond those points.

6. The importance of a homogeneous solution is stressed and the advantages of urea are discussed.

Quantitative Determination of Aluminum by Precipitation with Urea

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Aluminum can be accurately separated from large amounts of calcium, barium, magnesium, manganese, cobalt, nickel, zinc, iron, cadmium, and copper by precipitation as the dense basic succinate by boiling with urea the acid solution containing succinic acid. Hydrolysis of the urea forms ammonia gradually in a homogeneous solution, resulting in a pH of 4.2 to 4.6. Owing to the dense nature of the precipitate, it is easily filtered and washed and shows much less adsorption of other salts than does the precipitate obtained by the usual methods. The basic sulfate precipitated in this way is also dense, but the pH must be 6.5 to 7.5 and separations in certain cases are less satisfactory. The accuracy of separations made by the urea method is far superior to that obtainable by the use of ammonia. This is attributed to a combination of four important factors—a dense precipitate, a slow, uniform increase in pH, a homogeneous solution, and a low final pH.

IN PREVIOUS work (20) it was found that upon heating aluminum solutions containing sulfates to which urea had been added, the aluminum was precipitated as basic

sulfate in a dense and easily filterable form. This was due to the slow, uniform increase in pH caused by the gradual hydrolysis of the urea. The advantages of this method of precipitation in the separation of aluminum from other metals were indicated: (1) The solution is homogeneous, since no reagents are added during precipitation. (2) The precipitate is much less bulky, thus reducing the error due to adsorption and facilitating filtration and washing. (3) The pH of the solution is easily controlled and can never be higher in any part of the solution than the final value obtained. It is not surprising, therefore, that the application of this process to the separation of aluminum should yield results surpassing in accuracy those obtained by the usual methods. This paper describes such separations in which the aluminum was precipitated as basic sulfate and basic succinate. There is little doubt that other anions, which form dense precipitates such as benzoate, would give similar results. The solubility of the basic sulfate was found to be about the same as that of aluminum hydroxide (20), equivalent to 0.2 mg. of aluminum oxide per liter in the pH range 6.5 to 7.5.

Quantitative Determination of Aluminum by Precipitation as Basic Sulfate

MATERIALS USED. The aluminum metal was a special grade obtained from the Aluminum Company of America and contained 99.94 per cent of Al, 0.03 per cent of Si, 0.01 per cent of Ti, and 0.03 per cent of Fe. The latter two are, of course, always precipitated with the aluminum. The urea was a c. p. grade. Ammonium chloride was reagent quality material. Ammonium hydroxide was prepared by passing ammonia from a cylinder through a scrubbing bottle into redistilled water contained in a quartz flask.

PROCEDURE. Approximately 0.1 gram of the aluminum metal was weighed into 600-ml. beakers, tall-form, and dissolved in about 5 ml. of dilute hydrochloric acid, gently warming at the end to ensure complete solution. After diluting somewhat, dilute ammonium hydroxide was added until the solution became slightly turbid, then it was cleared with dilute hydrochloric acid, and one or two drops in excess were added. Four grams of urea, 20 grams of ammonium chloride, and 1 gram of ammonium sulfate were introduced and the volume was brought to 500 ml. The solution was then heated to boiling and kept gently boiling for 2 hours after the appearance of an opalescence, after which it was placed on an electric hot plate for 1 hour to allow the precipitate to settle. The precipitate was filtered off, and that adhering to the beaker removed as thoroughly as possible by means of pieces of filter paper.

To ensure complete removal of the last traces of the precipitate, it was dissolved in a little hydrochloric acid, reprecipitated by the procedure of Blum (2), and filtered through the paper containing the main portion of the precipitate. The combined precipitates were washed ten times with hot 1 per cent ammonium chloride solution, made alkaline to methyl red with ammonium hydroxide. After ignition to constant weight in a platinum crucible over a blast Meker at approximately 1200° C., it was weighed in a counterpoised weighing bottle. The pH of the filtrate and the amount of aluminum in the filtrate and washings, amounting to 0.078 to 0.1 mg., were determined colorimetrically (21).

Several workers (6, 10, 13, 14) have reported that sulfate which accompanies aluminum when it is precipitated as hydroxide from sulfate solutions, is very difficult to remove by ignition. An examination of the ignited oxide obtained above, by fusion with sodium carbonate and finally testing with barium chloride, showed that only a negligible amount of

TABLE I. QUANTITATIVE DETERMINATION OF ALUMINUM BY PRECIPITATION AS BASIC SULFATE

Final pH of Solution	Al ₂ O ₃ ^a Taken Gram	Al ₂ O ₃ Found Gram	Error Al ₂ O ₃ Mg.
7.08	0.1913	0.1916	+0.3
7.07	0.1954	0.1956	+0.2
7.03	0.1960	0.1957	-0.3
7.27	0.1950	0.1954	+0.4
6.77	0.1915	0.1912	-0.3
6.58	0.1909	0.1907	-0.2
7.09	0.1941	0.1940	-0.1
7.17	0.1920	0.1917	-0.3
6.94	0.1920	0.1921	+0.1
6.99	0.1914	0.1913	-0.1

^a Corrected for impurities in the original metal.

TABLE II. SEPARATION OF ALUMINUM FROM OTHER ELEMENTS
(Single precipitation)

Aluminum Taken Gram	Metal Added Gram	Amount Present in Precipitate Mg.
0.1	Ca ^a 1.0	Trace
0.1	Mg 1.0	None
0.1	Ni 0.125	0.7
0.1	Co 0.125	1.0
0.1	Zn 0.125	13.6
0.1	Mn 1.0	0.1
0.1	Cd 0.125	0.4
0.1	Cu 0.125	7.3

^a 0.5 gram of (NH₄)₂SO₄ used since 1 gram caused slight precipitation of CaSO₄.

sulfate was retained. Since the earlier work (20) indicated that the precipitate was relatively rich in sulfate, this shows that sulfate can be completely removed by igniting to a sufficiently high temperature (1200° C.). The results obtained by the above procedure are given in Table I.

SEPARATION OF ALUMINUM FROM CALCIUM, MAGNESIUM, NICKEL, COBALT, ZINC, MANGANESE, CADMIUM, AND COPPER. According to Lundell and Knowles (12), aluminum can be separated from the alkalis, alkaline earths, magnesium, and moderate amounts of manganese and nickel by precipitating according to the procedure of Blum (2). The separation from copper, cobalt, and zinc is not satisfactory, from 4 to 20 mg. remaining after one precipitation, and from 1 to 10 mg. after two, using 100 mg. of aluminum and 50 mg. of the accompanying element (9). From the analytical qualities of the precipitate obtained by the present method, considerably better separations might be expected.

It was found that when separate solutions containing 0.5 gram of nickel, cobalt, zinc, manganese, cadmium, and cop-

per as chlorides, together with 4 grams of urea and 1 gram of potassium sulfate were heated overnight on a hot plate, partial precipitation occurred. However, if the solutions contained 10 grams of ammonium chloride in addition to the above, no precipitate formed. The effectiveness of the separation of aluminum from these elements, and also from calcium and magnesium, was determined by precipitating the aluminum from individual solutions containing their chlorides, using the procedure described above. After filtering and washing, the precipitate was dissolved in hydrochloric acid, and the amount of accompanying element carried down was determined by an appropriate standard procedure. Table II gives the data obtained.

These results show that the separation of aluminum from calcium, magnesium, manganese, and cadmium, by a single precipitation with urea in the presence of sulfate, is satisfactory. Using this method only 0.1 mg. of manganese is carried down by 0.1 gram of aluminum in the presence of 1 gram of manganese, while with an ammonium hydroxide precipitation, 1.7 mg. of manganese accompanies the aluminum when these same amounts of the two elements are used. The separation from nickel, cobalt, zinc, and copper is not very good, although a single precipitation by this method is at least as effective with the last three of these elements as a double one with ammonium hydroxide.

Since the final pH values of the solutions were 6.7 to 7.0, which is about the same as that of Blum's method, it is probable that the greater purity of the precipitate obtained by the present method is due to the reasons mentioned above. The gradual increase in the pH of the solution, which is uniform throughout, allows the major part of the aluminum to be precipitated before the pH rises to a point where there is danger of precipitating the more basic elements.

Precipitation of Aluminum in the Presence of Succinate

PRELIMINARY INVESTIGATION. In the exploratory work on the influence of various anions on the quality of the precipitates obtained with urea, it was found that those formed in the presence of formate, oxalate, succinate, benzoate, and phthalate were dense, while that formed in the presence of acetate was flocculent (20). Several workers (1, 3, 15) have reported that the pH values at which hydroxides or basic salts begin to precipitate show some variation in the presence of different anions.

A series of determinations with different anions was made to determine the pH necessary for complete precipitation. Solutions of 500-ml. volume, containing approximately 0.1 gram of aluminum as chloride, 4 grams of urea, and 10 grams of ammonium chloride together with the amounts of the various salts shown in Table III, were heated in a boiling water bath until the appearance of a slight opalescence. The solutions were then rapidly cooled to room temperature and the pH was determined with a

quinhydrone electrode. The solutions were then gently boiled for 2 hours, the precipitate was filtered off, the filtrate tested for complete precipitation, and the pH determined.

Further study of the basic acetate method employed by Mittasch (16), Funk (7), and Kling, Lassieur, and Lassieur (11) failed to establish any conditions which would give a dense precipitate when the neutralization was caused by the hydrolysis of urea. The basic formate method (5, 8) modified by heating with urea was unsuccessful, as shown by attempts to precipitate aluminum in the presence of nickel. If enough formate was present to give a dense precipitate, the aluminum was incompletely precipitated, and that portion which did precipitate showed the presence of nickel. With 4 grams of ammonium formate in the solution, only about 60 per cent of the aluminum precipitated, while with 15 grams present, about 33 per cent came down. With much smaller amounts of formate, the beneficial effect of the anion on the quality of the precipitate was not realized. Work with the succinate showed that conditions which would give a dense precipitate and quantitative precipitation could be attained easily if succinic acid was added instead of sodium succinate, since the latter causes an immediate precipitate.

CONDITIONS FOR COMPLETE PRECIPITATION OF ALUMINUM IN THE PRESENCE OF SUCCINATE. It was found that the amount of succinate present affected not only the character of the precipitate but also the completeness of the precipitation,

TABLE III. INFLUENCE OF CERTAIN ANIONS ON THE pH OF FIRST OPALESCENCE AND COMPLETE PRECIPITATION

Anion	Salt Used	Salt Grams	pH at First Opalescence ^a	pH after 2 Hours	Precipitation
Phosphate	(NH ₄) ₂ HPO ₄ ^b	3	2.3	6.1 ^c	Complete
Succinate	Acid	5	3.6	4.0	Complete
Phthalate	KHC ₈ H ₄ O ₄	3	3.8	4.9	Complete
Sulfate	(NH ₄) ₂ SO ₄	1	4.2	6.5-7.5	Complete
Formate	HCOONa ^b	3	4.8	6.0	Incomplete
Acetate	NaC ₂ H ₃ O ₂ ^b	3	d	5.5	Complete

^a pH measured at room temperature, opalescence noted at boiling point.

^b Original solution contained sufficient hydrochloric acid to prevent formation of a precipitate while being brought to a boil.

^c Precipitation probably complete in less than 2 hours.

^d Precipitate flocculated too rapidly to allow determination of this value.

especially when other elements were present. Three grams of succinic acid and 10 grams of ammonium chloride in 500 ml. were sufficient to give a dense precipitate, and complete precipitation of aluminum when alone. However, if 0.15 gram of nickel or zinc was present, the precipitation of the aluminum was incomplete with 3 grams of succinic acid, but quantitative if 4 grams or 5 grams were used.

Since the pH of the solution and consequently the completeness of precipitation are dependent on the duration of boiling, this relationship was studied in a manner similar to the determination of the solubility of the basic aluminum sulfate precipitate. The solutions containing 0.1 gram of aluminum,

4 grams of urea, 5 grams of succinic acid, and 10 grams of ammonium chloride in 500 ml. were gently boiled, after the appearance of turbidity, for the lengths of time given in Table IV. The determinations were then completed as previously described (20).

This shows that for the complete precipitation of aluminum by heating with urea in the presence of succinate and ammonium chloride, it is necessary to boil gently for 1.5 to 2 hours after the appearance of turbidity, and that this procedure results in a pH of about 4.4.

Quantitative Determination of Aluminum by the Succinate Method

PROCEDURE. The aluminum solution was prepared as described in the basic sulfate method. After diluting somewhat, 5 grams of succinic acid dissolved in about 100 ml. of water were added, followed by 10 grams of ammonium chloride and 4 grams of urea. The solution was diluted, heated to boiling, and gently boiled for 2 hours after it had become turbid (40 to 45 minutes after it had commenced to boil). The precipitate was allowed to subside for a few minutes, and after a little paper pulp was added, it was filtered and washed ten times with a 1 per cent succinic acid solution, made neutral to methyl red with ammonium hydroxide. The precipitate adhering to the beaker was removed as in the basic sulfate method, except that in this instance the small precipitate obtained with ammonium hydroxide was filtered on a separate paper. The combined precipitates were ignited to constant weight in a platinum crucible at 1200° C. The pH of the filtrate was determined with a quinhydrone electrode, and the amount of aluminum remaining in the filtrate (approximately 0.1 mg.) and in the wash waters (negligible) was ascertained colorimetrically as before.

TABLE IV. EFFECT OF DURATION OF BOILING ON pH OF SOLUTION AND COMPLETENESS OF PRECIPITATION

Duration of Boiling ^a <i>Hours</i>	pH of Solution	Al ₂ O ₃ in Filtrate <i>Mg./l.</i>
0.25	3.30	<i>b</i>
0.5	3.58	1.2
1	3.93	0.8
1.25	4.01	0.8
1.5	4.15	0.2
2	4.40	0.2

^a After the appearance of turbidity.

^b Sufficient aluminum left in the filtrate to give a precipitate with ammonium hydroxide.

MODIFIED PROCEDURE. When the entire neutralization is dependent on the decomposition of urea, considerable time is consumed before precipitation commences, especially when an acid reducing agent is added as in the determination of copper, discussed later. To avoid this, a partial preliminary neutralization with dilute ammonium hydroxide was tried. When this reagent was slowly added to a cold solution containing urea, ammonium chloride, and succinic acid until barely turbid, a flocculent precipitate was rapidly formed on heating to boiling. However, if it was added dropwise to the hot solution to the point of faintest opalescence, the precipi-

tate obtained on further heating was entirely satisfactory. It was slightly more bulky than that obtained without preliminary neutralization, but was still compact enough to filter and wash rapidly. It had the distinct advantage of being more easily retained by the filter paper.

Since turbidity appears at approximately the pH at which bromophenol blue or methyl orange changes color, it is sometimes convenient to employ one of these as indicators. It is, of course, not necessary to neutralize to the point of turbidity, but it is very important not to overstep it, since this will cause the formation of a somewhat flocculent precipitate on further heating. Table V shows the results obtained using

TABLE V. QUANTITATIVE DETERMINATION OF ALUMINUM BY THE SUCCINATE METHOD

Volume Ml.	Duration of Boiling Hours ^a	pH of Solution ^b	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found Gram	Error Al ₂ O ₃ Mg.
500	2	4.43	0.1912	0.1911	-0.1
500	2	4.57	0.1906	0.1903	-0.3
500	2	4.44	0.1906	0.1906	±0.0
500	2	4.32	0.1931	0.1927	-0.4
500	2	4.26	0.1899	0.1899	±0.0
500	2	4.26	0.1899	0.1895	-0.4
500	2	4.48	0.1899	0.1896	-0.3
250	2	4.36	0.1911	0.1911	±0.0
250	2	4.22	0.1903	0.1900	-0.3
250	2	4.44	0.0957	0.0956	-0.1
250	2	4.31	0.0960	0.0958	-0.2
250	2	4.53	0.0059	0.0059	±0.0
250	2	4.50	0.0057	0.0056	-0.1
250	2	4.62	0.0025	0.0015	-1.0
250	2	4.53	0.0017	0.0005	-1.2
250	3	4.77	0.0021	0.0021	±0.0
250	3	4.94	0.0023	0.0023	±0.0
Modified Method					
250	0.5	3.76	0.1894	0.1887	-0.7
250	1	3.96	0.1897	0.1898	+0.1
500	1	4.01	0.1897	0.1898	+0.1
500	1	3.98	0.1905	0.1908	+0.3
500 ^c	1	4.00	0.1903	0.1907	+0.4
500 ^c	1	3.86	0.1909	0.1906	-0.3
500 ^d	1	3.98	0.1901	0.1900	-0.1
500 ^d	1	4.03	0.1906	0.1906	±0.0

^a After the appearance of turbidity.

^b At room temperature

^c Bromophenol blue used as indicator.

^d Methyl orange used as indicator.

both procedures. A correction was made for impurities in the metal.

Experiments on the ignition of the precipitate showed that heating for 1 hour at 1200° C. was sufficient to attain constant weight and to convert it into a nonhygroscopic (corundum) form which could be weighed directly in a covered crucible without the necessity of placing it in a covered weighing bottle. It was also found that Coors unglazed porcelain crucibles suffered no change in weight during such ignition and they were, therefore, used in place of platinum in most subsequent work.

It is evident that aluminum can be quantitatively precipitated by heating with urea in the presence of succinate and ammonium chloride for 1 to 2 hours after the appearance of

turbidity if 5 mg. or more are present, and that the time can be shortened by partial preliminary neutralization. With smaller amounts, about an hour longer is required. The resulting low pH, combined with the granular quality of the precipitate, the slow rate of precipitation, and the homogeneity of the solution, should allow much more satisfactory separations from the more basic elements than precipitation by ammonium hydroxide or even as the basic sulfate.

Separation of Aluminum from Other Metals

This method was applied to the separation of aluminum from a considerable number of other metals. In all cases the weight of aluminum taken was corrected for impurities. When a second precipitation was made, the basic succinate was dissolved from the filter into the same beaker by hot, dilute hydrochloric acid and the process repeated. The impurity in the oxide was determined by suitable methods.

DETERMINATION OF ALUMINUM IN THE PRESENCE OF CALCIUM, BARIUM, MAGNESIUM, MANGANESE, AND CADMIUM. These separations and determinations were made by a single precipitation from a volume of 250 ml. Table VI shows the results obtained, and indicates clearly that by this method a single precipitation from 250 ml. will satisfactorily separate approximately 0.1 gram of aluminum from 1 gram of the above elements.

DETERMINATION OF ALUMINUM IN THE PRESENCE OF NICKEL AND COBALT. Table VII shows the results obtained when this method is applied to the separation of aluminum from nickel and cobalt.

It is evident that one precipitation will effectively separate 0.1 gram of aluminum from an equal amount of cobalt or nickel or a few milligrams of aluminum from as much as 1 gram. A double precipitation gives a very satisfactory separation of 0.1 gram of aluminum from as much as 1 gram of these metals. This is a much better separation than that obtained by the use of ammonia, which, after one precipitation, leaves 0.6 mg. of nickel and 4.1 mg. of cobalt out of 50 mg. with the aluminum when one precipitation is made, and 1.2 mg. of cobalt after two precipitations (9).

DETERMINATION OF ALUMINUM IN THE PRESENCE OF COPPER. When this general procedure is applied to the determination of aluminum in the presence of copper, the separation is incomplete, owing to the relatively low solubility of cupric succinate. If, however, the copper is kept in the cuprous state, by the presence of a suitable reducing agent during the precipitation, the separation becomes entirely satisfactory, as the results given in Table VIII show.

When a reducing agent was used, 4 grams of hydroxylamine hydrochloride or 10 ml. of freshly prepared 2 *N* ammonium bisulfite and 10 grams of ammonium chloride were added to the aluminum chloride solution. It was diluted to about 150 ml. and heated to boiling to reduce the copper to the cuprous state.

When the solution had become colorless, 5 grams of succinic acid and 4 grams of urea were added, and the volume was brought to about 250 ml. Dilute ammonium hydroxide was added dropwise

TABLE VI. DETERMINATION OF ALUMINUM IN PRESENCE OF CALCIUM, BARIUM, MANGANESE, AND CADMIUM BY PRECIPITATION AS BASIC SUCCINATE

Element Added Gram	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found Gram	Element with Al ₂ O ₃ Mg.	Error Al ₂ O ₃ Mg.
1.0 Ca	0.1897	0.1895	None	-0.2
1.0 Ca	0.1905	0.1903	None	-0.2
1.0 Ca	0.1905	0.1904	None	-0.1
1.0 Ca	0.1903	0.1904	None	+0.1
1.0 Ba	0.1909	0.1908	None	-0.1
1.0 Ba	0.1905	0.1905	None	±0.0
1.0 Mg	0.1906	0.1904	None	-0.2
1.0 Mg	0.1906	0.1907	None	+0.1
1.0 Mg	0.1892	0.1894	None	+0.2
1.0 Mg	0.1894	0.1890	None	-0.4
1.0 Mn	0.1904	0.1906	0.3	+0.2
1.0 Mn	0.1904	0.1906	0.3	+0.2
1.0 Mn	0.0949	0.0950	0.25	+0.1
1.0 Mn	0.0949	0.0953	0.25	+0.4
1.0 Mn ^a	0.1903	0.1901	0.2	-0.2
1.0 Mn ^a	0.1906	0.1905	0.2	-0.1
0.5 Mn	0.1895	0.1897	0.2	+0.2
0.5 Mn	0.1890	0.1893	0.2	+0.3
1.0 Cd	0.1901	0.1901	<0.1	±0.0
1.0 Cd	0.1902	0.1900	<0.1	-0.2
1.0 Cd	0.1906	0.1907	<0.1	+0.1
1.0 Cd	0.1897	0.1897	<0.1	±0.0

^a Precipitated from 500 ml.

TABLE VII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF NICKEL AND COBALT BY PRECIPITATION AS BASIC SUCCINATE

Element Added Gram	Number of Pre- cipitations	Volume Ml.	Al ₂ O ₃ Taken * Gram	Al ₂ O ₃ Found Gram	Ni or Co in Al ₂ O ₃ Mg.	Error Al ₂ O ₃ Mg.
1.0 Ni	1	250	0.1903	0.1921	1.8	+1.8
1.0 Ni	1	250	0.1901	0.1919	1.8	+1.8
1.0 Ni	1	500	0.1905	0.1922	1.3	+1.7
1.0 Ni	1	500	0.1901	0.1918	1.2	+1.7
1.0 Ni ^a	1	500	0.1897	0.1913	1.0	+1.6
1.0 Ni ^a	1	500	0.1893	0.1910	1.0	+1.7
1.0 Ni	1	500	0.0049	0.0050	Trace	+0.1
1.0 Ni	1	500	0.0056	0.0057	Trace	+0.1
0.5 Ni	1	250	0.1919	0.1935	1.3	+1.6
0.5 Ni	1	250	0.1905	0.1923	1.6	+1.8
0.1 Ni	1	250	0.1901	0.1904	0.3	+0.3
0.1 Ni	1	250	0.1901	0.1903	0.3	+0.2
1.0 Ni	2	250	0.1903	0.1903	0.2	±0.0
1.0 Ni	2	250	0.1901	0.1903	0.3	+0.2
1.0 Ni	2	500	0.1895	0.1893	0.1	-0.2
1.0 Ni	2	500	0.1901	0.1902	0.2	+0.1
1.0 Co	1	250	0.1894	0.1919	1.9	+2.5
1.0 Co	1	250	0.1897	0.1924	2.0	+2.7
1.0 Co	1	500	0.1913	0.1932	1.2	+1.9
1.0 Co	1	500	0.1906	0.1925	1.2	+1.9
1.0 Co ^a	1	500	0.1906	0.1921	1.2	+1.5
1.0 Co ^a	1	500	0.1899	0.1914	1.2	+1.5
1.0 Co	1	250	0.0058	0.0058	Trace	±0.0
1.0 Co	1	250	0.0040	0.0043	Trace	+0.3
0.5 Co	1	250	0.0964	0.0977	0.8	+1.3
0.5 Co	1	250	0.0954	0.0963	0.6	+0.9
0.1 Co	1	250	0.0954	0.0954	0.2	±0.0
0.1 Co	1	250	0.0968	0.0971	0.3	+0.3
1.0 Co	2	250	0.1895	0.1896	0.1	+0.1
1.0 Co	2	250	0.1902	0.1904	0.1	+0.2
1.0 Co	2	250	0.1899	0.1903	0.1	+0.4
1.0 Co	2	250	0.1904	0.1902	0.1	-0.2

^a Modified procedure.

to the hot solution to incipient turbidity, and gentle boiling continued for 2 hours. The precipitate was filtered off while hot and washed with a hot solution containing per liter 10 grams of suc-

cinic acid and either 10 grams of hydroxylamine hydrochloride or 40 ml. of 2*N* ammonium bisulfite, the wash solution having been made neutral to methyl red with ammonium hydroxide. The determination was completed as described above.

The main points to be noted are that the copper must be completely reduced to the cuprous state, and the filtration and washing must be done hot.

These data show that aluminum can be very satisfactorily separated from large amounts of copper by a single precipitation, by heating with urea in the presence of succinate, ammonium chloride, and a suitable reducing agent. A double precipitation with ammonium hydroxide will usually leave as much as 8 mg. of copper out of 50 mg. with the aluminum, when precipitating 0.1 gram of the latter (9).

TABLE VIII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF COPPER

No.	Cu Added Gram	Reducing Agent	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found Gram	Cu in Al ₂ O ₃ Mg.	Error Al ₂ O ₃ Mg.
1	0.1	None	0.0947	0.0972	...	+2.5
2	0.1	None	0.0953	0.0976	...	+2.3
3	0.01	None	0.0945	0.0956	...	+1.1
4	0.01	None	0.0953	0.0960	...	+0.7
5	1.0	NH ₂ OH·HCl	0.1897	0.1901	0.1	+0.4
6	1.0	NH ₂ OH·HCl	0.1903	0.1901	0.1	-0.2
7	1.0	NH ₂ OH·HCl	0.0951	0.0952	None	+0.1
8	1.0	NH ₂ OH·HCl	0.0949	0.0952	None	+0.3
9	1.0	NH ₂ OH·HCl	0.0953	0.0953	None	±0.0
10	1.0	NH ₂ OH·HCl	0.0951	0.0950	None	-0.1
11	1.0	NH ₄ HSO ₃	0.1891	0.1888	0.05	-0.3
12	1.0	NH ₄ HSO ₃	0.1891	0.1891	0.05	±0.0

DETERMINATION OF ALUMINUM IN THE PRESENCE OF ZINC. The general procedure applied to the determination of aluminum in the presence of zinc gave the results shown in Table IX, which indicate that, even with as little as 10 mg. of zinc present, an appreciable amount is to be found with the aluminum after a single precipitation. Only 0.1 to 0.2 mg., however, is found to be present after two precipitations, when as much as 1 gram was originally present. The superiority of this method over the use of ammonium hydroxide is obvious from the fact that in the latter case as much as 10 mg. out of 50 mg. of the zinc may accompany the aluminum after two precipitations (9).

Since zinc metal is readily volatilized at elevated temperatures, it should be possible to remove the small amount which accompanies the aluminum by ignition in a current of hydrogen or with carbon.

A single precipitation was made in the usual manner from 500 ml. of solution containing 1.0 gram of zinc and approximately 0.1 gram of aluminum. When the ignition was to be made in the presence of carbon, some paper pulp was added before filtration. The precipitate was ignited in a covered unglazed porcelain crucible over a Meker blast, occasionally lifting the cover to allow the zinc to escape. After ignition for an hour in this manner, the cover was removed, the remainder of the carbon burned off, and the ignition completed in an electrically heated muffle for 1 hour at 1200° C. In determinations 3 to 6 (Table X), this oxide, after weighing, was ignited for 1 hour at 1000° to 1100° C.

over a Meker blast, in a current of hydrogen introduced through a silica Rose crucible cover and inlet tube. This treatment was followed by 1 hour at 1200° C. in the electric muffle. Determinations 7 to 10 were precipitated as described, but filtered without adding paper pulp. The filter paper was charred off and the oxide ignited in a stream of hydrogen, followed by 1 hour at 1200° C., as above.

The results, tabulated in Table X, show that the zinc carried down by the aluminum can be completely volatilized by heating the precipitate for 1 hour in a covered crucible in a

TABLE IX. DETERMINATION OF ALUMINUM IN THE PRESENCE OF ZINC

Zn Added Gram	Number of Precipitations	Volume Ml.	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found Gram	Zn in Al ₂ O ₃ Mg.	Error Al ₂ O ₃ Mg.
1.0	1	500	0.1909	0.1929	1.0	+2.0
1.0	1	500	0.1906	0.1928	1.0	+2.2
1.0 ^a	1	500	0.1903	0.1917	1.2	+1.4
1.0 ^a	1	500	0.1906	0.1920	1.2	+1.4
0.5	1	500	0.1901	0.1915	b	+1.4
0.5	1	500	0.1909	0.1923	b	+1.4
0.1	1	500	0.1903	0.1911	0.3	+0.8
0.1	1	500	0.1906	0.1914	0.3	+0.8
0.01	1	500	0.1901	0.1904	0.3	+0.3
0.01	1	500	0.1914	0.1918	0.3	+0.4
1.0	2	250	0.0953	0.0957	0.2	+0.4
1.0	2	250	0.0951	0.0952	0.2	+0.1
1.0	2	250	0.0955	0.0956	0.2	+0.1
1.0	2	250	0.0953	0.0955	0.2	+0.2

^a Modified procedure.

b Not determined.

TABLE X. SEPARATION OF ALUMINUM FROM ZINC PRECIPITATE IGNITED WITH CARBON AND/OR IN A CURRENT OF HYDROGEN

(1 gram of zinc present. Single precipitation, volume 500 ml.)

No.	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found after Igniting with Carbon Gram	Error Al ₂ O ₃ Mg.	Al ₂ O ₃ Found after Igniting in Hydrogen Gram	Zn in Al ₂ O ₃ Mg.	Error Al ₂ O ₃ Mg.
1	0.1892	0.1896	+0.4	...	...	...
2	0.1892	0.1894	+0.2	...	...	...
3	0.1905	0.1912	+0.7	0.1905	...	±0.0
4	0.1894	0.1895	+0.1	0.1893	...	-0.1
5	0.1899	0.1911	+1.2	0.1900	...	+0.1
6	0.1903	0.1917	+1.4	0.1903	...	±0.0
7	0.1903	...	...	0.1905	None	+0.2
8	0.1906	...	...	0.1906	None	±0.0
9 ^a	0.1909	...	...	0.1907	None	-0.2
10 ^a	0.1890	...	...	0.1889	None	-0.1

^a Single precipitation from 250 ml.

current of hydrogen. This makes it possible to determine aluminum in the presence of large amounts of zinc by a single precipitation, following the given procedure.

The failure to remove the zinc by igniting with carbon may be due to the absence of any gas stream to sweep out the volatilized metal.

DETERMINATION OF ALUMINUM IN ZINC-BASE DIE-CASTING ALLOYS. These alloys contained about 2.8 per cent of copper and 92.5 per cent of zinc with very small amounts of lead, cadmium, magnesium, and iron.

A 1-gram sample of the alloy was dissolved in sufficient hydrochloric acid to be equivalent to about 10 grams of ammonium chloride, adding a few crystals of potassium chlorate at the end to obtain complete solution. Most of the free acid was neutralized with ammonium hydroxide, 0.1 to 0.2 gram of hydroxylamine hydrochloride was added, and the solution heated (see "Determination of Aluminum in the Presence of Copper"). Dilute ammonium hydroxide was added until the precipitate redissolved with difficulty, then 4 grams of urea and 5 grams of succinic acid were introduced and the volume was brought to about 250 ml.

When the solution had gently boiled for 2 hours after becoming turbid, the liquid was decanted through a filter paper containing a small amount of paper pulp. The precipitate was washed by decantation a few times with a solution containing 1 per cent succinic acid and 0.01 per cent hydroxylamine hydrochloride, and made neutral to methyl red with ammonium hydroxide. It was then dissolved in hydrochloric acid; 10 grams of ammo-

TABLE XI. DETERMINATION OF ALUMINUM IN A ZINC-BASE DIE-CASTING ALLOY

No.	Sample	Number of Precipitations	Volume Ml.	Sample Taken Grams	Al ₂ O ₃ Found Gram	Al Found %	Al Present %
1	A	2	250	1.001	0.0738	3.91	3.92 ^a
2	A	2	250	1.002	0.0739	3.90	3.92
3	A	2	250	1.002	0.0739	3.90	3.92
4	A	2	250	1.000	0.0739	3.91	3.92
5	B	2	250	1.001	0.0739	3.91	3.92
6	B	2	250	1.002	0.0737	3.89	3.92
7	B	2	250	1.002	0.0744	3.93	3.92
8	B	2	250	1.002	0.0742	3.92	3.92
9	C	2	250	1.002	0.0747	3.94	3.94 ^b
10	C	2	250	1.002	0.0742	3.92	3.94
11	A	1	500	1.004	0.0739	3.90	3.92 ^a
12	A	1	500	1.002	0.0738	3.90	3.92
13 ^c	A	1	500	1.001	0.0739	3.90	3.92
14 ^c	A	1	500	1.001	0.0741	3.92	3.92
15	A	...	...	2.001	0.1470	3.89	3.92
16	A	...	...	2.000	0.1490	3.95	3.92
17	A	...	...	2.001	0.1470	3.89	3.92
18	A	...	...	2.002	0.1473	3.89	3.92

^a Bureau of Standards analysis. Not a standard sample.

^b 3.94% Al by Gooch-Havens method using a 10-gram sample.

^c No. 13 ignited with carbon gave 3.90% Al, while No. 14 gave 3.95% Al.

nium chloride, 4 grams of urea, and 5 grams of succinic acid were added, and it was reprecipitated in a volume of 250 ml. The solution was filtered through the original paper, and the precipitate adhering to the beaker removed as before described. The precipitates were ignited together in an unglazed porcelain crucible, first at a low temperature to char off the paper and finally for 1 to 1.5 hours at 1200° C. in an electrically heated muffle. The first ten determinations in Table XI were made in the above manner.

Determinations 11 to 14 were made by the modified procedure. The samples were prepared and the reagents added as before. The solution was diluted to about 500 ml., and heated to boiling and dilute ammonium hydroxide was added dropwise to incipient turbidity. After gentle boiling for 1 hour, the precipitate was filtered off and washed, and the last traces were removed from the beaker as usual. The filter paper was charred off in an unglazed porcelain crucible, and the oxide was ignited for 1 hour in a current of hydrogen, then 1 hour at 1200° C. in air.

For the purpose of comparison, determinations 15 and 16 were made by the method of Craighead (4), in which zinc, copper, etc., are removed by electrodeposition at a mercury cathode. Numbers 17 and 18 were made using a combination of the mercury cathode method, followed by a double precipitation by the present method.

These results show that small percentages of aluminum can be accurately determined in a commercial alloy containing a large per cent of zinc by either of the two methods given.

DETERMINATION OF ALUMINUM IN THE PRESENCE OF IRON. Since ferric iron begins to precipitate at a pH of approximately 2, it is obvious that for any separation of aluminum as a basic salt the iron must be in the ferrous state, under which conditions it commences to precipitate at a pH of 5.5 (3). With the present method of precipitation, the final pH of the solution is seldom above 4.5, which should allow an excellent separa-

TABLE XII. EFFECTIVENESS OF REDUCING AGENTS ON THE SEPARATION OF ALUMINUM FROM IRON BY PRECIPITATION AS BASIC SUCCINATE

No. Taken	Fe Grams	No. of Pptns.	Reducing Agent ^a	Al ₂ O ₃ Taken Gram	Al ₂ O ₃ Found, Corrected for Fe ₂ O ₃ Gram	Fe ₂ O ₃ in Pptn. Mg.	Error Al ₂ O ₃ Mg.
1	1.0	1	5 grams Na ₂ S ₂ O ₃ ·5H ₂ O	0.1910	0.1912	3.0	+0.2
2	1.0	2	5 grams Na ₂ S ₂ O ₃ ·5H ₂ O	0.1904	0.1902	0.2	-0.2
3	1.0	2	5 grams Na ₂ S ₂ O ₃ ·5H ₂ O	0.1918	0.1922	0.4	+0.4
4	1.0	2	5 grams Na ₂ S ₂ O ₃ ·5H ₂ O	0.1918	0.1918	0.5	±0.0
5	1.0	2	5 grams Na ₂ S ₂ O ₃ ·5H ₂ O	0.1897	0.1898	0.4	+0.1
6	1.0	1	{ 5 grams Na ₂ S ₂ O ₃ ·5H ₂ O 0.5 ml. phenylhydrazine	0.1893	0.1893	2.2	±0.0
7	1.0	1	1.5 grams sodium hydrosulfite	0.1889	0.1920	1.3	+2.1
8	1.0	1	1.5 grams sodium hydrosulfite	0.1894	0.1941	1.8	+4.7
9	1.0	2	4 grams NH ₂ OH·HCl, 25 mg. Cu	0.1903	0.1897	.	-0.6
10	1.0	2	3 grams NH ₂ NH ₂ ·2HCl, 25 mg. Cu	0.1913	0.1915	0.4	+0.2
11	1.0	2	3 grams NH ₂ NH ₂ ·2HCl, 25 mg. Cu	0.1903	0.1901	0.4	-0.2
12	1.0	2	3 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1901	0.1907	0.5	+0.6
13	1.0	2	3 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1903	0.1911	0.5	+0.8
14 ^b	0.05	1	2 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1892	0.1890	0.5	-0.2
15 ^b	0.05	1	2 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1892	0.1888	0.4	-0.4
16	1.0	2	3 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1943	0.1944	0.8	+0.1
17	1.0	2	3 grams NH ₂ NH ₂ ·H ₂ SO ₄	0.1898	0.1897	0.6	-0.1
18	1.0	1	{ 3 grams NH ₂ NH ₂ ·H ₂ SO ₄ 0.5 ml. phenylhydrazine	0.1900	0.1896	1.9	-0.4
19	1.0	2	3 grams <i>p</i> -aminophenol	0.1895	0.1882	0.3	-1.3
20	1.0	2	3 grams <i>p</i> -aminophenol	0.1934	0.1915	0.3	-1.9
21	1.0	2	3 grams <i>p</i> -aminophenol	0.1908	0.1898	0.4	-0.9
22	1.0	2	3 grams <i>p</i> -aminophenol hydrochloride	0.1891	0.1888	0.4	-0.3
23	1.0	2	3 grams <i>o</i> -aminophenol hydrochloride	0.1910	0.1904	0.2	-0.6
24	1.0	2	3 grams <i>o</i> -aminophenol hydrochloride	0.1899	0.1852	0.2	-4.7
25	0.02	1	3 grams hydroquinone	0.1912	0.1913	0.5	+0.1
26	1.0	2	2 grams hydroquinone	0.1889	0.1890	0.2	+0.1
27	1.0	2	3 grams hydroquinone	0.1894	0.1893	0.3	-0.1
28	1.0	2	2 grams hydroquinone	0.1898	0.1901	0.4	+0.3
29	1.0	2	3 grams hydroquinone	0.1905	0.1903	0.25	-0.2
30	1.0	2	3 grams hydroquinone	0.1920	0.1923	0.3	+0.3
31	1.0	2	3 grams hydroquinone	0.1912	0.1914	0.3	+0.2
32	1.0	2	3 grams hydroquinone	0.1905	0.1907	0.3	+0.2
33	2.0	2	3 grams hydroquinone	0.0433	0.0433	0.35	±0.0

^a Same reducing agent used in second precipitation.

^b Precipitation and filtration made in an atmosphere of carbon dioxide.

tion of aluminum from ferrous iron. This would require the presence of a reducing agent which is stable enough to withstand the rather extended time of heating and yet strong enough to keep the iron completely reduced. The reducing agents sodium thiosulfate, ammonium bisulfite, sodium hydrosulfite, phenylhydrazine, hydroxylamine hydrochloride plus a little copper as catalyst (19), hydroquinone, *p*-aminophenol, *o*-aminophenol, and *p*-anisidine were examined for this purpose.

The procedure was similar to that employed in the determination of aluminum in the presence of copper. The amount of electrolytic iron shown in the tables was dissolved in hydrochloric

acid and added to the aluminum chloride solution. After reducing the iron as completely as possible by adding fresh ammonium bisulfite to the hot solution, the ammonium chloride, urea, succinic acid, and reducing agent were introduced. The solution was diluted to 500 ml., heated to boiling, and neutralized to incipient turbidity with ammonium hydroxide, and the determination was completed as usual, washing the precipitate with a solution of 1 per cent succinic acid and a little of the reducing agent, made neutral to methyl red with ammonium hydroxide. Whenever a double precipitation was made, the first precipitate was dissolved in hydrochloric acid and the process repeated. The iron accompanying the aluminum was determined colorimetrically with thiocyanate after fusion of the ignited oxide with potassium pyrosulfate.

TABLE XIII. DETERMINATION OF ALUMINUM IN THE PRESENCE OF IRON

(2 ml. of phenylhydrazine added as reducing agent in each precipitation)

Fe Taken <i>Grams</i>	No. of Pptns.	Al ₂ O ₃ Taken <i>Gram</i>	Al ₂ O ₃ Found, Corrected for Fe ₂ O ₃ <i>Gram</i>	Fe ₂ O ₃ in Pptn. <i>Mg.</i>	Error Al ₂ O ₃ <i>Mg.</i>
0.01	1	0.19325	0.19350	0.13	+0.25
0.02	1	0.19035	0.19030	0.13	-0.05
0.035	1	0.18980	0.18980	0.26	±0.00
0.05	1	0.18975	0.19020	0.50	+0.45
0.05	1	0.19125	0.19110	0.30	-0.15
0.135	1	0.18965	0.18955	0.60	-0.10
1.0	1	0.19060	0.19085	1.15	+0.25
1.0	2	0.19060	0.19050	0.09	-0.10
1.0	2	0.19835	0.19850	0.15	+0.15
2.0	2	0.03985	0.03970	0.07	-0.15
2.0	2	0.05735	0.05755	0.13	+0.20
2.0	2	0.02360	0.02355	0.10	-0.05

Several methods were attempted to remove the iron from the ignited oxide, but no particular success was attained. Ignition of the impure oxide for 1 hour in a current of hydrogen, followed by extraction with hot concentrated hydrochloric acid, failed to remove all the iron and at the same time dissolved from 0.1 to 0.2 mg. of aluminum. Repeated heating of the ignited oxide in an air bath with a mixture of ammonium chloride and ammonium bromide (17, 18) showed that the process was inefficient and of doubtful analytical value for the present purpose. Representative results of this preliminary work are given in Table XII, while Table XIII shows the results obtained using phenylhydrazine as reducing agent.

Tables XII and XIII show that phenylhydrazine is the best suited of any of the above-mentioned reducing agents for keeping the iron reduced, and preventing it from being precipitated with aluminum by urea from a solution containing succinate and ammonium chloride. This is probably due to its tendency to volatilize with steam, thus maintaining a reducing atmosphere above the liquid. In all cases where 1 gram of iron was present, a rust-colored rim of precipitate formed on the wall of the beaker at the surface of the liquid during the first precipitation. This was much less pronounced with phenylhydrazine than with any of the others. If the solution has a volume of approximately 500 ml., the presence of 2 ml. of phenylhydrazine will give a satisfactory separation of 0.1 gram of aluminum from

0.2 gram of iron in a single precipitation. If more iron is present, reprecipitation is necessary. A double precipitation will separate 0.1 gram of aluminum from 1 gram of iron, or 0.03 gram from 2 grams of iron.

Hydroquinone was not quite as effective, 0.2 to 0.4 mg. of ferric oxide usually remaining after two precipitations. Hydroxylamine appeared to keep the iron reduced while the solution was appreciably acid but as the pH value became high enough for the complete precipitation of aluminum, the iron readily oxidized. This would seem to confirm the views of Solaja (19) that ferric iron is easily reduced by this reagent in acid solution, while in alkaline solution ferrous iron is readily oxidized by it.

Sodium thiosulfate, sodium hydrosulfite, and hydrazine sulfate and hydrochloride did not prove at all satisfactory, since they failed to keep the iron reduced or prevent its oxidation at the surface of the liquid. Both *o*- and *p*-amino-phenol gave consistently low results for aluminum and at the same time were not particularly good for preventing the precipi-

TABLE XIV. DETERMINATION OF ALUMINUM IN IRON ORE

No.	Wt. of Sample Grams	Al ₂ O ₃ Present %	Al ₂ O ₃ Found %	Error %	Phos- phorus Present %	Phos- phorus in Ppt. %
1	3.0370	1.01	0.73	0.28	0.09	0.037
2	4.8573	1.01	0.95	0.06	0.09	0.031
3	3.4992	1.01	0.98	0.03	0.09	0.028
4	3.6156	1.01	0.98	0.03	0.09	0.031
5	3.2485	1.01	0.95	0.06	0.09	0.087
6	2.8595	1.01	1.00	0.01	0.09	0.081

tation of iron. *p*-Anisidine and ammonium bisulfite proved to be so valueless that no final determinations were made with them.

The above procedure was applied to the determination of aluminum in Bureau of Standards iron ore No. 26, containing 1.01 per cent of Al₂O₃, 0.07 per cent of TiO₂, and 0.09 per cent of P₂O₅. The ore was dissolved with hydrochloric acid, the silica was removed and volatilized in the usual way, and the residual oxides were added to the main solution. The iron was reduced, phenylhydrazine added, and the aluminum precipitated twice according to the above procedure. After weighing the aluminum oxide it was fused with potassium pyrosulfate, the iron and titanium were precipitated by cupferron, and the iron was determined colorimetrically. The phosphorus in the filtrate was determined. The weight of the precipitate was corrected for these impurities. The results are shown in Table XIV.

In Nos. 5 and 6 ammonium sulfate was added instead of succinate, in the hope of obtaining more complete precipitation of phosphorus and aluminum. It is obvious that the method tends to give results which are slightly low. It is possible that some phosphorus was lost in the fusion with pyrosulfate, but it is certain that in the succinate method not all is retained by the precipitate. This was also true when 0.1 gram of aluminum was added to the ore, the recovery in

this case being about 60 per cent of the total, whereas by the sulfate method the precipitation of phosphorus was complete.

Attempts were made to precipitate aluminum as phosphate by the use of urea. Although the precipitate filtered exceptionally well, the results were erratic and always too high by 1 to 15 mg., regardless of whether sulfate, succinate, or neither was present. It is probable that some of the aluminum, precipitated while the solution is still rather acid, forms an acid phosphate.

A preliminary study of the effect of various anions on the precipitation of other weak bases showed that while sulfate invariably caused the formation of a dense precipitate, there was no uniformity in the action of other anions.

The method has already yielded good results in the case of gallium. If titanium is present it is quantitatively precipitated with the aluminum. By a suitable modification of this method to be described in a later paper it has been found possible to separate titanium from aluminum. The quantitative precipitation of other bases is being investigated.

Summary

It has been found that aluminum can be quantitatively precipitated at a pH of 6.5 to 7.5 by gently boiling for 1 or 2 hours after the appearance of turbidity, its solution containing 4 grams of urea, 10 or 20 grams of ammonium chloride, and 1 gram of ammonium sulfate. A single precipitation gives a very good separation of 0.1 gram of aluminum from 1 gram of calcium, magnesium, and manganese, while the separation from nickel, cobalt, zinc, and copper is much superior to that obtained by the use of ammonia.

The substitution of succinate for sulfate makes the precipitation of aluminum quantitative at a pH of 4.2 to 4.6, from a solution otherwise of similar composition. If the hot solution is first neutralized to incipient turbidity with dilute ammonia, the time required may be considerably shortened without much change in the character of the precipitate.

By this method a single precipitation will effectively separate 0.1 gram of aluminum from an equal amount of nickel or cobalt, or from 1 gram of calcium, barium, magnesium, manganese, and cadmium, or a few milligrams of aluminum from 1 gram of cobalt or nickel. If the final oxide is ignited in a current of hydrogen to volatilize zinc, one precipitation will also serve to separate 0.1 gram of aluminum from 1 gram of zinc. A double precipitation will give an excellent separation of the same quantity of aluminum from 1 gram of nickel, cobalt, or zinc.

The separation from copper in one precipitation is successful if a suitable reducing agent is present to keep the copper in the cuprous state. Iron must also be kept in the ferrous form and phenylhydrazine was found to be the best for this

purpose. Two precipitations give a good separation of 0.1 gram of aluminum from 1 gram of iron or of 0.03 gram of aluminum from 2 grams of the latter, but any phosphate present is only partially precipitated. Aluminum can be accurately determined in a zinc-base die-casting alloy containing large amounts of zinc and some copper.

Aluminum phosphate precipitated by this method contains excess of phosphate. The success of this method depends on the slow increase in pH caused by the decomposition of the urea, resulting in a dense precipitate, a homogeneous solution, and a low final pH.

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